

ISOBUTANOL COUPLING WITH ETHANOL AND METHANOL TO ETHERS OVER SULFONATED RESIN CATALYSTS: ACTIVITIES AND SELECTIVITIES

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ABSTRACT

The synthesis of C_3 - C_8 ethers from mixtures of C_1 - C_4 alcohols over strong acid Amberlyst resin catalysts has been initiated, and the overall activity pattern of the resins was found to be Amberlyst-35 > Amberlyst-36 > Amberlyst-15 > Amberlyst-1010, all of which were more active than Nafion-H. With methanol/isobutanol reactants, it was observed that increasing the reaction pressure strongly decreased the space time yield and selectivity of the butenes, principally isobutene, while tending to increase the space time yield of the ethers methylisobutylether (MIBE), methyl tertiarybutyl ether (MTBE), and dimethylether (DME). Other reactant mixtures utilized at high flow rates included ethanol/isobutanol, where EIBE and ETBE were products. Upon increasing the isobutanol/ethanol ratio above 1/1, it was shown that diethylether (DEE) formation decreased but the synthesis of tertiarybutyl isobutylether (TBIBE) increased. A reactant mixture of ethanol/isopropanol was also investigated, and dehydration of the isopropanol readily occurred to form propene and coupling gave diisopropylether (DIPE) as the dominant product at 90°C.

INTRODUCTION

The objective of this research program is to explore new pathways for synthesizing high value oxygenates, e.g. fuel-grade ethers, from non-petroleum feedstocks. In particular, the development of catalysts and processes for converting alcohols produced from coal- or natural gas-derived $H_2/CO/CO_2$ synthesis gas is being pursued. Alkali-doped Cu/ZnO-based catalysts produce a mixture of alcohols from H_2/CO , and this mixture consists principally of methanol and isobutanol [1-6]. The synthesis of ethers from these two alcohols has been shown to occur by the direct coupling of methanol and isobutanol over strong acid catalysts, and the observed dominant products were MIBE at moderate pressures and a mixture of methanol and isobutene at low pressures [7,8]. This research has now been extended to ethers containing the ethyl and isopropyl groups instead of the methyl moiety.

EXPERIMENTAL

The Amberlyst solid acid resin catalysts, designated as Amberlyst-15, -35, -36, and -1010, were obtained from Rohm and Haas. These catalysts have similar polymeric structures, but the Amberlyst-35 and -36 resins are more thermally stable (up to $\approx 140^\circ C$) and have higher acidity (5.2 and 5.4 meq/g dry, respectively) than the commonly utilized Amberlyst-15 resin (4.7 meq/g dry), while the Amberlyst-1010 has a much higher surface area ($\approx 540 \text{ m}^2/\text{g}$), smaller average pore size (5 nm rather than 20-30 nm), and lower concentration of acid sites (3.3 meq/g dry). Aqueous ion exchange titrations here with 0.5 NaOH confirmed the number of acid sites as stated by the manufacturer. The swelling properties of the dried (to $90^\circ C$) resins in water and in methanol were also determined, and it was observed that the Amberlyst-15, -35, and -36 resins swelled 42-58%, while the Amberlyst-1010 swelled 22-25% (the two liquids induced similar swelling behavior).

The catalysts were subjected to a standard test for ether synthesis in a downflow stainless steel bench-scale reactor system that is automated for continuous operation, as previously described [9,10]. The alcohols were injected at the top of the reactor in a preheated zone by means of a high pressure Gilson pump and an ISCO piston pump provided by Air Products and Chemicals, Inc. The carrier gas consisted of He containing 18.5% of N_2 . The conversion and product composition were monitored by continual sampling of the exit stream by GC analysis using in-line, heated, automated Valco sampling valves [10]. The initial experimental conditions are as follows:

Catalyst weight	5.0 g dry resin	Methanol feed	1.72 mol/kg cat/hr
Temperature	90°C	Isobutanol feed	1.72 mol/kg cat/hr
Total pressure	1 atm (0.1 MPa)	He/ N_2 carrier	16 mol/kg cat/hr

RESULTS

Activities and Selectivities of the Amberlyst Catalysts. Testing of the catalysts was carried out under steady state conditions at each temperature, and the data were tabulated as averages during 3-15 hr runs for each set of reaction parameters. Comparison of the conversions of the alcohols at 90°C is made in Table 1. Upon increasing the reaction temperature sequentially in 10°C increments to 130°C, the activity increased with each catalyst. Since the Amberlyst-35 resin was the most active catalyst, the stability of the catalyst was investigated. Table 2 shows that no deactivation was observed during this 50 hr test, and, therefore, testing at 130°C did not cause destruction nor fouling of the resin.

Selectivity data were compiled for all catalytic tests, but only those for the Amberlyst-35 catalyst will be presented here. Under the reaction conditions employed, the catalysts were generally rather non-selective, especially at the lower temperatures. The Amberlyst-1010 tended to exhibit higher selectivity toward DME than did the other Amberlyst resins. As shown in Figure 1, Amberlyst-35 mainly formed butenes at 90-110°C, but at 120°C and above DME was predominantly formed.

Pressure Dependence Study of Amberlyst-35. The reaction of methanol and isobutanol over a Nafion-H catalyst has previously been shown to be very sensitive to the total pressure [7,8]. To investigate the pressure dependence of the synthesis reaction over Amberlyst-type catalysts, the active Amberlyst-35 resin was chosen. The total reaction pressure was varying while maintaining a constant reactant flow rate. The experiment was carried out using the following conditions:

Catalyst weight	1.0 g dry catalyst	Methanol feed	10.4 mol/kg cat/hr
Temperature	90 and 117°C	Isobutanol feed	5.2 mol/kg cat/hr
Total pressure at		He + N ₂	185 mol/kg cat/hr
90°C	0-79 psig (0.1-0.64 MPa)		
117°C	0-180 psig (0.1-1.3 MPa)		

Similar trends in selectivities were observed for the two reaction temperatures, and demonstrated that the formation of butenes (generally ≈85% of the butenes consisted of isobutene) was very sensitive to the alcohol partial pressure, e.g. Figure 2. Thus, a small elevation of the alcohol pressure suppressed the formation of butenes rather drastically, while the synthesis rates of DME, MIBE, and MTBE ethers were affected much less significantly, although there was a trend to increase the space time yield of these ethers as the alcohol pressure was increased.

Coupling Reactions of Ethanol with Isobutanol and Isopropanol. The coupling reactions of ethanol with isobutanol and isopropanol were investigated over the Amberlyst-35 catalyst at 90°C and 1 MPa under a wide range of conditions; in particular the relatively low conversion levels were usually maintained so that the data could subsequently be incorporated into a kinetic and mechanistic model of ether synthesis over this catalyst. The lower conversion levels were achieved by utilizing high GHSV.

Table 3 shows the conversions and product selectivities from ethanol/isobutanol = 1/1 and 1/3 reactant mixtures at 110°C. The higher level of isobutanol tended to decrease the overall alcohol conversion and the selectivity toward DEE. However, it significantly increased the selectivity toward the formation of TBIBE. Decreasing the ethanol/isobutanol ratio to 1/5 and the temperature to 100°C decreased the reaction rates even more but increased the selectivity to TBIBE, as well as of the isobutene (Table 4). For comparison, the data obtained for the methanol/isobutanol reaction at 110°C are shown in Table 5. Similar selectivity trends are noted by comparing Tables 3 and 5.

Studies have also been carried out with ethanol/isopropanol reactant mixtures at high flow rates, and an example of the data is given in Table 6. It is evident that isopropanol is quite reactive, in particular with respect to dehydration to form propene and DIPE, which has a blending octane number of 105 [10]. In addition, much more ethylisopropylether (EIKE) than DEE is formed. It is expected that high yields of these ethers could be formed by using much lower gas flow rates.

CONCLUSIONS

The strong acid Amberlyst resins are active for the synthesis of ethers and olefins from mixtures of alcohols. With the exception of Amberlyst-36, the activity of the macro-

reticular Amberlyst catalysts at 90°C correlated with the content of the strong acid sites, with Amberlyst-35 being the most active, and differences in selectivity patterns were observed. With methanol, ether products consisted of DME, MIBE, MTBE, and isobutene (with ethanol, analogous ethyl products were formed), and it was shown that increasing reaction pressure greatly decreased the selectivity toward isobutene. With ethanol/isobutanol reactants at 1 MPa over Amberlyst-35, tertiarybutylisobutylether (TBIBE) was a significant product, and this ether should have desirable fuel properties. In an experiment with ethanol/isopropanol = 1/1.6 reactants, it was shown that isopropanol was more reactive than ethanol and formed propene and DIPE, as well as EIPE.

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TABLE 1. Activity of the polymeric resin catalysts at 90°C

Catalyst	% Methanol Conversion	% Isobutanol Conversion
Amberlyst-15	9.1	10.2
Amberlyst-35	16.4	15.8
Amberlyst-36	12.3	10.2
Amberlyst-1010	5.0	4.2

TABLE 2. Amberlyst-35 activity as a function of reaction temperature.

Temperature (°C)	% Methanol Conversion	% Isobutanol Conversion
90	16.4	15.8
100	32.1	43.9
110	42.9	63.9
120	62.0	57.1
130	70.0	57.9
90	17.0	15.7

TABLE 3. Activity and selectivity for the conversion of ethanol and isobutanol (10.3/10.4 and 10.3/31.2 mol/kg cat/hr) to products over the Amberlyst-35 catalyst (1 g) at 110°C and 1.1 MPa with total flow rate of 516 mol/kg cat/hr

Product	Conversion (mol%)	Selectivity (%) Based on Ethanol	Selectivity (%) Based on Isobutanol
Ethanol	12.3, 7.4		
Isobutanol	10.2, 4.1		
DEE		63.1, 42.7	
ETBE		2.1, 4.0	2.5, 2.3
EIBE		34.8, 53.4	41.4, 31.2
Isobutene			37.9, 33.9
TBIBE			8.6, 22.0
DIBE			5.8, 7.4

TABLE 4. Activity and selectivity for the conversion of ethanol and isobutanol (14/69 mol/kg cat/hr) to products over the Amberlyst-35 catalyst (0.5 g) at 100°C and 1.1 MPa with total flow rate of 575 mol/kg cat/hr

Product	Conversion (mol%)	Selectivity (%) Based on Ethanol	Selectivity (%) Based on Isobutanol
Ethanol	1.7		
Isobutanol	1.8		
DEE		16.6	
ETBE		5.2	1.2
EIBE		78.2	17.7
Isobutene			42.1
TBIBE			29.0
DIBE			10.0

TABLE 5. Activity and selectivity for the conversion of methanol and isobutanol (22.8/26.0 and 7.6/26.0 mol/kg cat/hr) to products over the Amberlyst-35 catalyst (1 g) at 110°C and 1.1 MPa with total flow rate of 524 mol/kg cat/hr

Product	Conversion (mol%)	Selectivity (%) Based on Methanol	Selectivity (%) Based on Isobutanol
Methanol	8.3, 9.8		
Isobutanol	4.3, 5.8		
DME		63.9, 38.0	
MTBE		3.7, 8.1	6.3, 4.0
MIBE		32.4, 53.9	55.7, 26.62
Isobutene			18.2, 39.8
TBIBE			12.4, 21.0
DIBE			7.4, 8.6

TABLE 6. Activity and selectivity for the conversion of ethanol and isopropanol (40/64 mol/kg cat/hr) to products over the Amberlyst-35 catalyst (0.5 g) at 90°C and 1.1 MPa with total flow rate of 596 mol/kg cat/hr

Product	Conversion (mol%)	Selectivity (%) Based on Methanol	Selectivity (%) Based on Isobutanol
Ethanol	1.4		
Isopropanol	4.0		
DEE		14.4	
EIPE		85.6	18.4
Propene			32.1
DIPE			49.5

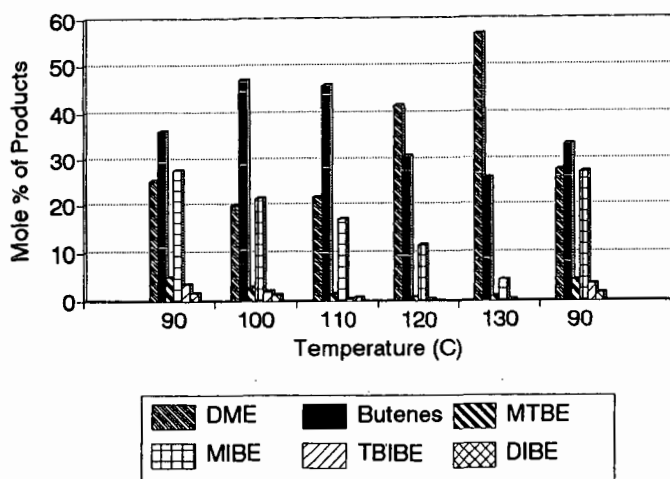


FIGURE 1. The selectivities of the products formed at different temperatures over the Amberlyst-35 resin at 0.1 MPa from a methanol/isobutanol = 1/1 reactant mixture.

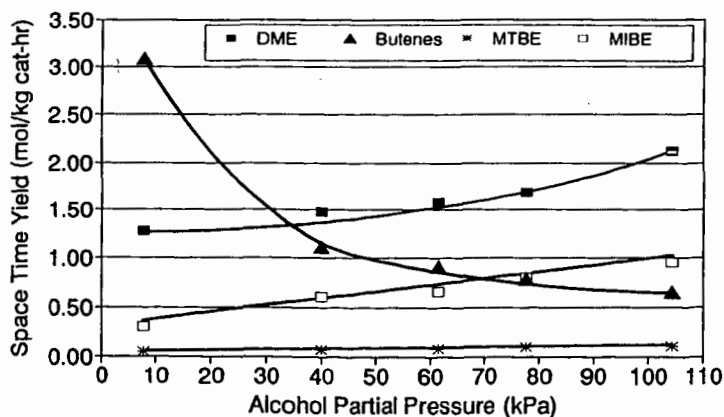


FIGURE 2. Space time yields of the ethers and butenes (mainly isobutene, but also including *trans*-2-butene and *cis*-2-butene) formed over the Amberlyst-35 catalyst as a function of the alcohol partial pressure at 117°C (methanol/isobutanol = 2/1).